

April 26, 1960

J. H. HIGHBERGER ET AL

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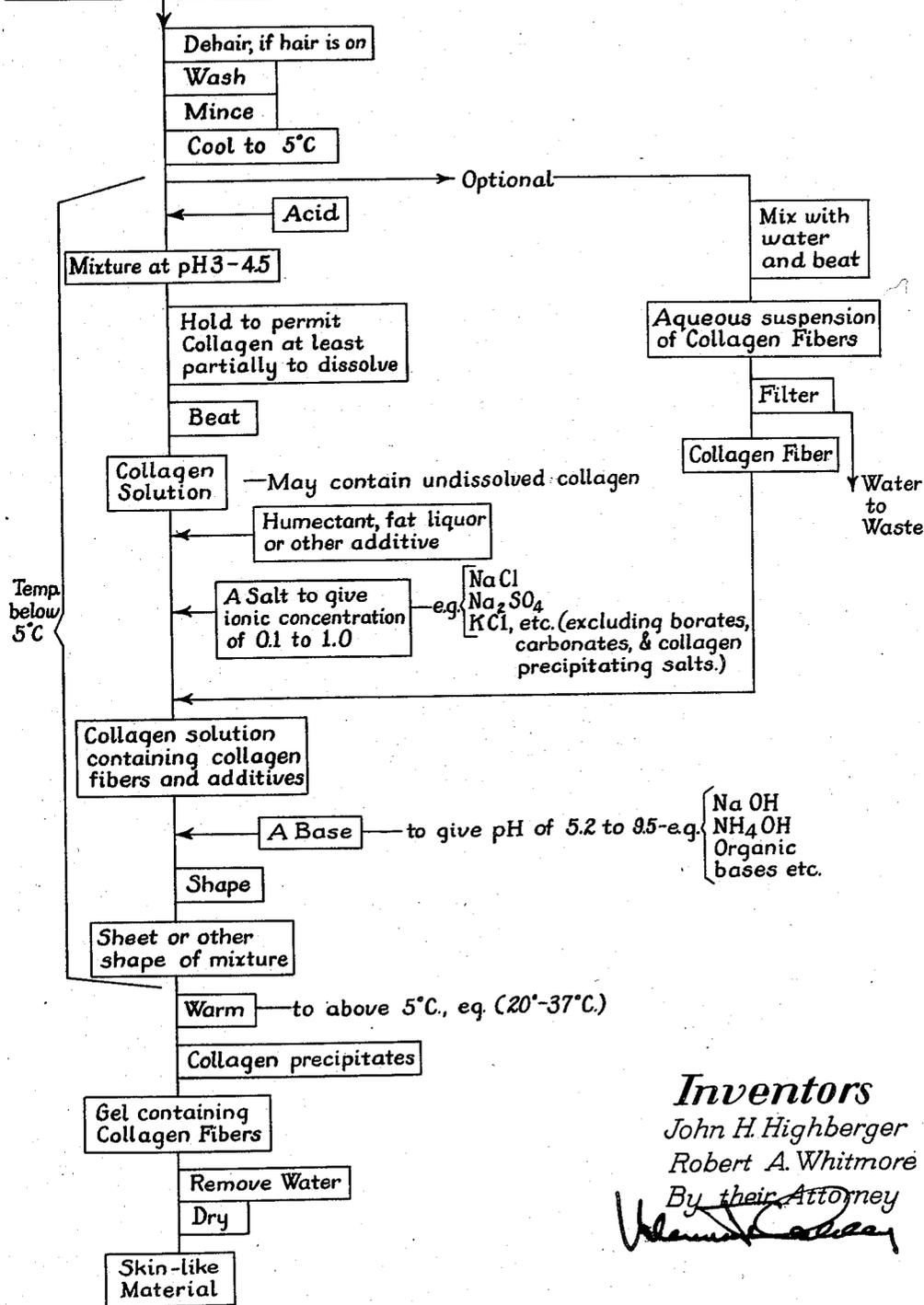
COLLAGEN FIBER MASSES AND METHODS OF MAKING THE SAME

Filed Dec. 21, 1955

2 Sheets-Sheet 1

Collagen Source eg Animal Fleshings, Skin, Trimmings

Fig. 1



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2 Sheets-Sheet 2

Fig. 2

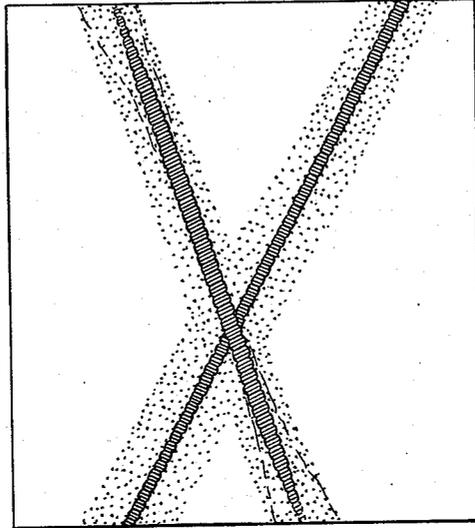
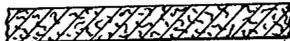


Fig. 3



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**COLLAGEN FIBER MASSES AND METHODS OF
MAKING THE SAME**

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10 Claims. (Cl. 106—155)

This invention relates to the preparation of collagen fiber masses, particularly to the preparation of sheet material convertible to a leather-like condition.

Skin and leather are composed of fibers of a protein called collagen. These fibers are arranged in a randomly interwoven three-dimensional network, and the ultimate properties of the leather depend upon this fact and upon the chemical nature of the fibers themselves and of the product formed by the treatment of the fibers with a tanning agent.

Leather possesses outstanding properties of toughness, abrasion resistance and high water vapor transfer rate together with a desirable appearance. Unfortunately, the skins from which leather is prepared are irregular in shape and thickness so that there is a high percentage of waste. The waste material has been of very little value and has been disposed of in such uses as fertilizers or has been used in making such products as leather board, that is an imitation leather material in which the scraps are pasted and pressed together into sheets. These leather board sheets lack the interwoven three-dimensional network which gives to leather its strength and other desirable properties.

Efforts have been made to develop a sheet material from the fibers of skin material by swelling the skin, mechanically breaking down the swollen skin and forming the resultant paste into sheets or threads. In these efforts, the net effect is to degrade the collagen of the skin to an extent that portions of it are converted into glue which holds other portions together. This material has a hard, non-fibrous feel as might be expected due to the glued together nature of the product; and the product is not a randomly interwoven three-dimensional network of fibers having the character of leather.

It is a feature of the present invention to provide a fibrous material and a simple process for making it in which collagen fibers are arranged in a randomly interwoven three-dimensional network capable of conversion to a leather-like fibrous material.

The invention will be described further in connection with the drawings, in which:

Fig. 1 is a flow sheet of the process of the present invention;

Fig. 2 is a reproduction of an electron micrograph of collagen material formed in the process; and

Fig. 3 is a cross section of a skin-like material produced according to the present invention.

It has been found that interwoven collagen fiber masses may be formed by mechanical subdivision of skin material followed by at least partial solution of the collagen content of the skin as undegraded collagen and thereafter reprecipitation of the collagen in the form of true collagen fibrous material. As shown in the flow sheet (Fig. 1) solution of the collagen content of skin or the like is effected in an aqueous bath under conditions of acidity and low temperature which dissolve the collagen without substantially degrading it. After the collagen dissolves, the ionic strength of the solution is adjusted

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to a special range, the solution is made neutral or slightly alkaline, and the collagen is precipitated from solution by raising the temperature of the solution. In the resultant product the collagen content is present in the form of true collagen fibers in a three-dimensional interwoven network. There is some indication that where undissolved collagen fibers are present in the bath they are integrated with the collagen fibers formed by precipitation of dissolved collagen. The precipitated fibrous product is initially in the form of a swollen gel from which the fluid is removed to form a product closely resembling animal skin and convertible to a leather-like product by the action of tanning agents.

The skins or skin scraps constituting raw material for the present invention may be any of the various waste skin materials discarded in the normal manufacture of leather. A preferred raw material is so-called hide cellar scraps which are abundant and cheap. Limed scraps from tanneries can also be used but must first be neutralized and washed or treated with a chelating agent to remove calcium ions from the material. These materials are treated to remove the hair, for example by liming or "sweating" and wiping off the loosened hair. The de-haired material is then mechanically subdivided and dispersed in a cold acidic aqueous bath for dissolving the collagen.

The subdivision of the skin may involve a mincing of the un-haired skin, for example in a power meat grinder, to a particle size not substantially larger than about $\frac{3}{16}$ " to $\frac{1}{4}$ " in diameter. Mincing may be effected without previous treatment or, if desired, the skin may be swelled before mincing, for example by a treatment in an acid bath having a pH of from about 3 to 5.2 for a period of, for example, six hours, or by liming and subsequent delimiting, to make the skin more readily broken up.

If desired, the skin may be swelled before comminuting by placing it in the acid bath in which the collagen is to be dissolved until the skin swells, removing and comminuting the swelled skin, and returning the comminuted skin to the bath. The skin is usually swelled satisfactorily for comminuting in about six hours, but may be left in the bath longer since any collagen dissolved will be recovered from the bath in later stages.

The minced or comminuted material is dispersed in an aqueous, acid, collagen-dissolving bath which is adjusted to have a pH of from 3 to 4.5, preferably from 3.5 to 4, and which is kept at a temperature of not over 5° C. Adjustment of the mixture of skin particles and acidic bath to most desirable conditions for dissolving collagen is ordinarily obtained by adding the wet hide particles to water containing somewhat less acid than will ultimately be required and, after preliminary mixing, bringing the pH to the desired value by addition of further acid. Usually one part by weight of the wet hide particles will be mixed with at least one and ordinarily from two to six parts by weight of acid solution. Any acid may be used which does not precipitate protein, and acetic acid, hydrochloric acid, sulfuric acid and other common organic and mineral acids have been used. A desirable acid solution is a ½% by weight acetic acid. After addition of skin particles to this acid and mixing, the pH is brought to the desired value by adding concentrated acid.

The proportion of skin particles to acid bath is determined in part by the mixing and beating equipment available. With mixing apparatus of the type similar to a Hollander machine used in preparing paper pulp it may be necessary to have as much as four to six parts by weight of water to one part by weight of the skin to permit functioning of the machine. With heavier mixing equipment, as little as one to two parts of acid solution to one part by weight of skin can be employed. The acid bath

containing skin material and preferably after a period sufficient to allow partial solution of the collagen, may be vigorously agitated and subjected to a beating action to break up larger skin fragments to enable the acid solution more readily to effect solution of the collagen content.

The extent of solution and the character of the ultimate product depend on the time allowed for action of the acid bath on the skin. Some solution occurs after six hours and products may be made from this partially dissolved material. It is preferred to continue the acid treatment to allow 24 to 48 hours' solution time and longer periods may be used. Mixing is continued until all of the fibers are swelled and the material brought to a translucent, relatively stiff fluid or paste.

In the fluid or paste obtained after mixing and agitation, a substantial proportion of the collagen of the skin is dissolved in undegraded form. If the fluid or paste is filtered through fine media, the filtrate is a solution which shows no trace of collagen fibers under the electron microscope at the highest magnifications; but normal collagen fibers can be precipitated from the solution. Examination of the fluid or paste itself under an electron microscope shows collagen fibers which give evidence under the electron microscope (see Fig. 2) of being surrounded by a shell or tube of nonfibrous material which, it seems reasonable to assume, is a viscous layer of at least partially dissolved collagen localized around the collagen fiber from which it originated.

Because of the localizing of dissolved collagen around collagen fibers it is not possible to state quantitatively the percent of collagen dissolved. However, as a rule of thumb, it has been found that desirable leather-like fibrous material can be obtained through the subsequent steps of the process if as little as 1/20% by weight of the liquid separable from the bath by filtration is precipitable in the form of normal collagen fibers. This value of mobile dissolved collagen is sufficient to cooperate with the collagen fibers to knit the mass together into a strong skin-like product when subjected to precipitation in the further steps of the process.

A tanning agent may be added to the mixture containing dissolved collagen. On subsequent precipitation of the mixture, there is obtained a leather-like body or sheet of tanned collagen fibrous material.

It has also been found that a skin-like or leather-like material is obtainable by combining finely divided skin in an acid bath at pH 3 to 4.5 with collagen solution in quantity to provide for the mixture an amount of precipitable collagen equal to 1/20% by weight of the resultant mixture.

The fluid or pasty collagenous material whether prepared by acid treatment of skin particles to dissolve collagen or prepared by mixing dissolved collagen with finely divided skin is adjusted as to ionic concentration by addition of a salt to a value between 0.1 to 1.0, preferably 0.4 to 0.6, and is treated with basic agents to raise its pH to a value of from 5.2 to 9.5, the temperature of the fluid being maintained below 5° C.

These ionic strength and pH ranges are important to successful formation of fiber sheets, for, if the ionic strength is low, precipitation occurs almost immediately on neutralization and if the ionic strength is high the gel formed does not synerese well, the fibers may be melted together and the gel may be reversible. At low pH values, the fibers do not knit together but form as individual fibers, and at high pH values the fibers do not form satisfactorily.

The following is the formula employed to derive the value of ionic strength:

Ionic strength

$$\frac{\text{molarity (of each ion)} \times \text{valence}^2 \text{ (of each ion)}}{2}$$

For example, the ionic strength of a 1 molar solution of calcium chloride

$$\text{Ca}^{++}\text{Cl}_2 = \frac{1 \times 2^2 + 1 \times 1^2 + 1 \times 1^2}{2}$$

To adjust the ionic strength, the normal additive is sodium chloride, but other inorganic salts such as sodium sulfate and potassium chloride are useful. Salts of which the cations are known to precipitate collagen are excluded and the borates and carbonates have been found to interfere with the process.

Basic agents useful to neutralize the material include NaOH, Na₃PO₄, Na₂HPO₄, ammonia, organic amines and so on. Buffer salts may be employed to aid in providing a closer control of the final pH.

Water soluble acid or direct dyestuffs in aqueous solution may be added to the collagenous material preferably after addition of chrome tanning agent where this is used.

It has been found desirable to incorporate a humectant, for example sorbitol, in the collagenous material. It has also been found that a fat liquor, which may, for example, be an emulsion of Neatsfoot oil, may be incorporated with the fluid or paste either before or after neutralization. The amount of fat liquor incorporated will depend upon the results desired in the final product and may be, for example, in the range of from 1% to 10% based on the weight of the fluid or paste. The fat liquor and/or humectant is incorporated by suitable mechanical mixing means.

Additional fibrous material, for example, various textile fibers such as cotton, nylon, etc., may also be incorporated in the fluid or paste while the fluid or paste is cold.

The fluid or paste with or without added material is then brought to the desired shape, for example by casting in a mold or spreading on a surface. Where the fluid or paste is relatively stiff it may be rolled out on a surface which optionally may have a surface pattern, or the material after being spread on a surface may be passed under a roll which will impress a desired pattern such as a grain on the surface of the deposited material.

The temperature of the fluid or paste is now raised above 5° C. preferably rather slowly. Ordinarily this warming is satisfactorily carried out by allowing the deposited material to reach room temperature, e.g. from 20° to 37° C., preferably from 22° to 25° C. in the course of several hours. The warming must not raise the temperature of the deposited material to above 37° C. During warming, the fluid or paste gels. The time of gelling depends in some measure on the ionic strength of the fluid or paste. Gelling occurs most rapidly at the low or high extremes of ionic strength within the range indicated and at temperatures of 37° C. gelation may occur in as little as five minutes. At an ionic strength of 0.1 gelation may begin at about 15° C. Gelation at ionic strengths of 0.4 to 0.6 may require several hours but will give a stronger, more satisfactory fibrous product.

The gelled material may be dried by any of various means. For example, drying may occur by simple evaporation from the surfaces of the gel, or the material may be dried under light pressure between absorbent surfaces, or drying may be effected by organic solvent action, as for example by the water-removing action of acetone.

In the course of drying, the gel shrinks to an extent determined by the initial water content of the gel. Where the initial water content was from 50% to 60% by weight, the dried material may be a little more than one-half as thick as the initial thickness of the gel. It has been found desirable to maintain a light pressure on the gel during drying to obtain a product of the highest uniformity. The product after drying preferably contains about 15% moisture.

The dried product bears a close resemblance to animal skin (see Fig. 3). Under the microscope it is found that the product is a three-dimensional network of fibers; and

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the fibers on examination under the electron microscope were found to be structured collagen. Where undissolved fibers were incorporated with dissolved collagen, the undissolved fibers are held in a three-dimensional network by the reconstituted collagen fibers which form a network or continuum holding the entire structure together. The relation of the fibers in products containing undissolved collagen fibers suggests that the undissolved fibers may serve as seed crystals into which collagen from solution may be deposited and actually grow in the process of gelation.

Where a tanning agent has not been incorporated in the mixture before precipitation, the dried fibrous sheet material may be subjected to any of the conventional tanning treatments employed for the treatment of natural skin, for example the fibrous material may be tanned with chromium tanning agents or vegetable tanning agents or with synthetic tanning agents to form products resembling leather.

The following examples are given for purposes of illustration to aid in understanding the invention and it is to be understood that the invention is not restricted to the particular conditions, proportions and reagents set forth therein.

Example I

Fresh calfskin corium (prepared by removing the epidermis from calfskin by shaving) was minced in a meat grinder to reduce it to pieces from approximately $\frac{3}{16}$ " to $\frac{1}{4}$ " in diameter and of the thickness of the skin. One kilogram of the corium particles was cooled to about 5° C. and introduced into a container; and 4 liters of $\frac{1}{2}$ % acetic acid at a temperature of about 0° C. were stirred into the skin material. The pH of this material was about 3.5. The container and its contents were kept at from 0° to 1° C. for 24 hours. At the end of 24 hours, the acid had swelled and partially dissolved the calfskin corium particles and the material was run through a mixing and beating device for a period of 30 minutes to form a soft paste. The mixing and beating device was similar to a Hollander machine employed in paper making and includes a tank in which is mounted drum carrying blades. The blades are disposed to pass in close relation to the bed plate when the drum is rotated to provide a severe mixing and beating action. The resultant paste was removed from the mixing device at a temperature of about 3° C. and was kept at this temperature until the final stage of the process.

A sample of the cold (3° C.) acid paste was filtered and a 100 gm. portion of the filtrate was adjusted to an ionic concentration of .4 by addition of 2.3 gms. of sodium chloride and was neutralized by adding 1 N sodium hydroxide to bring the pH to 7.5 as determined by indicator paper. The temperature of the neutralized filtrate was then raised uniformly over a period of 6 hours to 25° C. At the end of this time a white opaque gel had formed. The gel was broken up and filtered to separate a fibrous mass. The fibrous mass was dried at room temperature to a moisture content of 15% and weighed. The dried weight of the fibers was 0.2 gram, that is, approximately 0.20% by weight of the liquid from which the fibers were precipitated. On electron microscope examination, the fibers were found to be typical collagen fibers.

A kilogram of untreated calfskin corium particles at about 5° C. was introduced into the mixing and beating device along with sufficient water to form a free flowing slurry. The mixer was started and beating and agitation of the material was continued for 30 minutes. At the end of this time the mixture had been converted into a flowable fibrous suspension. Water was removed by filtering the suspension through cloth and the filtered material was pressed between sheets of cloth to bring the solids content to approximately 60% as determined by drying a sample of the material to constant weight at room tem-

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perature under vacuum over P₂O₅. The fibrous material was stored at temperatures below 5° C.

1200 gms. of the cold 60% solids fibrous material were mixed with 33.6 gms. of sodium chloride to bring the ionic strength within the necessary range and thereafter 50 gms. of d-sorbitol were kneaded in. To this mixture, 200 gms. of the cold acid paste were added and blended in. The mass was brought to pH 7.5 (as determined by indicator paper) by addition of 1 N sodium hydroxide solution and the mass was spread out on a glass plate to a thickness of approximately $\frac{1}{4}$ ". A second glass plate was placed on the layer and the assembly was allowed to warm to room temperature overnight. The sheet shrank in thickness and limited syneresis occurred. The upper glass plate was then removed and the sheet was allowed to air dry. The dried product was approximately $\frac{1}{8}$ " thick and was a tough, flexible sheet resembling untanned animal skin. The sheet was found to have a three-dimensional network of fibers when examined under an optical microscope. The fibers in the dried product showed typical collagen structure in the electron microscope.

The dried sheet material was subjected to a conventional chrome tanning process and formed a product resembling leather.

Example II

Commercial limed and dehaired steer hide scrap was washed and was then minced in a meat grinder to reduce it to pieces from approximately $\frac{3}{16}$ " to $\frac{1}{4}$ " in diameter. The ground material was again washed and was brought to a pH of about 5 by addition of glacial acetic acid. The material was chilled to about 0° to 1° C. and then introduced into the mixing and beating machine with sufficient fresh water to form a free flowing slurry and was beaten for 10 minutes to form a fibrous suspension, the temperature being kept below about 5° C. during this operation. Water was removed from the suspension by filtering the suspension through a cloth bag filter and pressing the bag to form a fibrous body having a solids content of about 20%. 1200 grams of this 20% solids fibrous material were mixed with 35 grams of d-sorbitol and the material stored at below about 5° C.

200 grams of the cold, acid, pasty material resulting from the acid treatment of calfskin by the procedure given in Example I were blended at 3° C. with 250 cc. of a cold (5° C.) 20% solution of a chrome tanning agent. The particular chrome tanning agent was a commercial sugar-reduced 31% basic, chrome sulfate tanning agent containing 24% by weight of Cr₂O₃ on the dry basis.

The resultant cold, pasty material containing tanning agent was mixed and blended with 1200 grams of the cold 20% solids fibrous material containing sorbitol. Thereafter the blended material was neutralized to pH 7.5 by addition of NaOH.

The neutralized material was spread out in a $\frac{1}{4}$ " thick layer and its temperature permitted to rise over a period of about 24 hours. Gelation of the material was observable when the temperature of the material had reached about 15° C. The gelled material was permitted to dry by simple evaporation and in the course of drying the gelled material shrank to a thickness approximately one-half the initial thickness of the gel. The dried sheet material resembled tanned leather.

It is to be observed that in this example, the chrome tanning agent supplies the ionic concentration required to insure proper gelation of the composition.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. A method for forming interlocked collagen fiber masses comprising the steps of comminuting skin, dispersing the comminuted skin and at least partially dissolving the collagen content of the skin in an aqueous bath at a pH of 3 to 4.5 and temperature of not over about 5° C., adjusting the ionic strength of the bath and

neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.1 to 1.0 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, thereafter raising the temperature of the bath sufficient to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, and removing fluid from the gel to reduce it to a body of interlocked collagen fibers.

2. A method for forming interlocked collagen fiber masses comprising the steps of comminuting skin, dispersing the comminuted skin in an aqueous bath at a pH of 3.5 to 4.0 and temperature of not over about 5° C. to dissolve at least a portion of the collagen content of the skin, beating the dispersion to break up collagen fiber bundles, adjusting the ionic strength of the bath and neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.1 to 1.0 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, thereafter slowly raising the temperature of the bath to about 20° C. to 35° C. to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, and removing fluid from the gel to reduce it to a body of interlocked collagen fibers.

3. A method for forming interlocked collagen fiber masses comprising the steps of comminuting skin, dispersing the comminuted skin in an aqueous bath at a pH of 3.5 to 4.0 and a temperature of not over about 5° C. to dissolve at least a portion of the collagen content of the skin, beating the dispersion to break up collagen fiber bundles, adding a tanning agent to the bath, adjusting the ionic strength of the bath and neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.4 to 0.6 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, thereafter slowly raising the temperature of the bath to about 20° C. to 35° C. to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, and removing fluid from the gel to reduce it to a tanned body of interlocked collagen fibers.

4. A method for forming interlocked collagen fiber masses comprising the steps of comminuting skin, dispersing the comminuted skin in an aqueous bath at a pH of 3.5 to 4.0 and a temperature of not over about 5° C. to dissolve at least a portion of the collagen content of the skin, adding and dispersing mechanically disintegrated collagen fibrous material to the bath, adjusting the ionic strength of the bath and neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.4 to 0.6 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, thereafter slowly raising the temperature of the bath to about 20° C. to 35° C. to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, and removing fluid from the gel to reduce it to a body of interlocked collagen fibers surrounding said added fibrous material.

5. A method for forming interlocked collagen fiber masses comprising the steps of comminuting skin, dispersing the comminuted skin in an aqueous bath at a pH of 3.5 to 4.0 and a temperature of not over about 5° C. to dissolve at least a portion of the collagen content of the skin, adding a humectant to the bath, adjusting the ionic strength of the bath and neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.4 to 0.6 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, thereafter slowly raising the temperature of the bath to about 20° C. to 35° C. to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, and removing fluid from the gel to reduce it to a body of interlocked collagen fibers.

6. A method for forming interlocked collagen fiber masses comprising the steps of comminuting skin, dispersing the comminuted skin in an aqueous bath at a pH of 3.5 to 4.0 and a temperature of not over about 5° C. to dissolve at least a portion of the collagen content of the skin, adding a fat liquor to the bath, adjusting the ionic strength of the bath and neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.4 to 0.6 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, thereafter slowly raising the temperature of the bath to about 20° to 35° C. to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, and removing fluid from the gel to reduce it to a body of interlocked collagen fibers.

7. A method for forming interlocked collagen fiber masses comprising the steps of swelling skin material by soaking it in an aqueous bath at a pH of 3 to 6 at a temperature of not over 5° C., comminuting the swollen skin, dispersing the comminuted skin in an aqueous bath at a pH of 3.5 to 4.0 and temperature of not over about 5° C. to dissolve at least a portion of the collagen content of the skin, adjusting the ionic strength of the bath and neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.4 to 0.6 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, thereafter slowly raising the temperature of the bath to about 20° to 35° C. to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, and removing fluid from the gel to reduce it to a body of interlocked collagen fibers.

8. A method for forming a leather-like material comprising interlocked collagen fiber masses comprising the steps of swelling skin material by soaking it in an aqueous bath at a pH of 3 to 6 at a temperature of not over 5° C., comminuting the swollen skin, dispersing the comminuted skin in an aqueous bath at a pH of 3.5 to 4.0 at a temperature of not over about 5° C. to dissolve at least a portion of the collagen content of the skin, mixing into the bath a humectant and a fat liquor, adjusting the ionic strength of the bath and neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.4 to 0.6 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, spreading the material in a sheet of substantially uniform thickness, thereafter slowly raising the temperature of the bath to about 20° C. to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, removing fluid from the gel to reduce it to a body of interlocked collagen fibers, and subjecting the resultant body to tanning conditions of the type used in the treatment of animal skins and hides.

9. A method for forming interlocked collagen fiber masses comprising the steps of comminuting skin, dispersing the comminuted skin in an aqueous bath at a pH of 3.5 to 4.0 at a temperature of not over about 5° C. to dissolve at least a portion of the collagen content of the skin, mixing into the bath a water soluble dyestuff, adjusting the ionic strength of the bath, and neutralizing the acid by addition of a basic agent to bring the bath to an ionic strength of 0.4 to 0.6 and pH in the range of 5.2 to 9.5 while maintaining the bath at temperatures not over about 5° C. to prevent precipitation of collagen, spreading the material in a sheet of substantially uniform thickness, thereafter slowly raising the temperature of the bath to about 20° C. to 35° C. to precipitate collagen fibers from dissolved collagen in the bath and to form a gel, and removing fluid from the gel to reduce it to a body of interlocked collagen fibers.

10. An animal skin-like mass consisting essentially of interlocked structured collagen fibers arranged in a ran-

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domly interwoven three-dimensional network and comprising both collagen fibers derived directly from skin, and collagen fibers formed on said directly derived fibers by precipitation from collagen solution.

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